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13. ABSTRACT (Maximum 200 words)

A theoretical/computational research program to develop methods, simulate complex reactions, and investigate the fundamental chemical dynamics of reactions of nitramine energetic materials occurring under various experimental conditions has been carried out. The focus of the research was on RDX (hexahydro-1,3,5-trinitro-s-triazine), however, the reactions of several related systems were studied. While the goal of the research was to develop accurate models for and a better understanding of the reactions of cyclic nitramines, the work has extended and improved the theoretical and computational methods for treating rate processes in complicated molecules and systems of molecules. Since the goal was realistic simulations of the reaction dynamics, the formulation of accurate potential energy surfaces was a crucial part of the work. We have developed methods for formulating accurate surfaces by using limited amounts of empirical and *ab initio* results. Classical methods were used in order to realistically treat the full dimensionalities of the systems. Reaction rates were calculated by using classical trajectory simulations, diffusion theory, and Monte Carlo variational transition-state theory. Semiclassical methods were developed to treat multidimensional effects in proton tunneling.

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CHEMICAL DYNAMICS STUDIES OF REACTIONS IN ENERGETIC MATERIALS

FINAL TECHNICAL REPORT

(Report Period: September 1, 1993 - August 31, 1997)

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Abstract

A theoretical/computational research program to develop methods, simulate complex reactions, and investigate the fundamental chemical dynamics of reactions of nitramine energetic materials occurring under various experimental conditions has been carried out. The focus of the research was on RDX (hexahydro-1,3,5-trinitro-*s*-triazine), however, the reactions of several related systems were studied. While the goal of the research was to develop accurate models for and a better understanding of the reactions of cyclic nitramines, the work has extended and improved the theoretical and computational methods for treating rate processes in complicated molecules and systems of molecules. Since the goal was realistic simulations of the reaction dynamics, the formulation of accurate potential energy surfaces was a crucial part of the work. We have developed methods for formulating accurate surfaces by using limited amounts of empirical and *ab initio* results. Classical methods were used in order to realistically treat the full dimensionalities of the systems. Reaction rates were calculated by using classical trajectory simulations, diffusion theory, and Monte Carlo variational transition-state theory. Semiclassical methods were developed to treat multidimensional effects in proton tunneling.

I. Statement of the Problem

The purpose of this research project was to investigate the chemical dynamics of key elementary reactions in mechanisms for the decomposition of cyclic nitramines. The studies were performed by developing theoretical/computational methods for treating complex chemical reactions involving large polyatomic molecules and performing accurate simulations of reactions in energetic materials. Of central interest is RDX (hexahydro-1,3,5-trinitro-s-triazine) with the focus on accurate descriptions of the initial decomposition reactions of RDX.

II. Summary of Results.

A. Methods.

The theoretical methods being developed in this research program have broad applications since they can be used to perform accurate simulations of chemical and physical processes in a wide variety of large systems that extend well beyond those of interest in this program. Many of the studies involve classical trajectory simulations.[1] The nature of systems in this program require that we employ classical methods in order to realistically treat the full dimensionalities of the problems. We have also developed a general computer code that allows us to efficiently model a wide range of systems with only minor investments of time for programming. We have recently written a detailed review of the methods we use.[2] While classical trajectory simulations are central to this research, other methods are needed to augment them in order to obtain complete descriptions of the reactions for all of the conditions of interest.

Most unimolecular reactions are accurately described by statistical theory at energies near threshold. We have developed a Monte Carlo variational transition-state theory (MCVTST) approach[3,4] for conditions where molecular dynamics calculations are not feasible. The MCVTST approach can be used without the approximations for the potential energy surface (PES) that are required in many statistical theories, and it can properly (within the classical approximation) include the multidimensional features of the statistical dynamics. This is an efficient, practical, and accurate method for computing statistical rates of reactions in large systems.[4]

The main advantage of the classical trajectory approach is that it allows one to simulate the details of processes, thus providing insight into the nature of the dynamics. However, since the calculations must often be performed at relatively high energies, where reaction rates may be controlled by the rate of intramolecular vibrational energy redistribution (*i.e.*, IVR-limited), there is a "gap" between the range of the trajectory results and the statistical regime (*i.e.*, near threshold). We have developed a new method, based on diffusion theory (*i.e.*, a classical master equation) approach, that can be used to accurately predict the rates of reactions in the IVR-limited regime; we call this method *intramolecular dynamics diffusion theory* (IDDT).[5-7] This is a practical method for predicting reaction rates in the non-statistical energy regime by using short-time classical trajectory results as input. This approach requires very little computer time compared to a direct simulation of a reaction, and is quite accurate.

The combination of the classical trajectory, MCVTST, and IDDT methods allow us to fully describe the reaction dynamics over the entire energy range of interest.

An important component of the work is the development of realistic PESs that describe molecules and their reactions both in isolation and in solids. We have used model, empirical, and *ab initio*-based potentials in our studies, depending on the particular problem of interest. We have developed methods for formulating complex PESs using a minimum of information so that simulations can be done for systems where it is difficult of have a lot experimental or *ab initio* information to define the PES. We have also developed schemes for making use of *ab initio* methods in formulating PESs.

B. Simulations and Calculations

Our research during the previous grant period consisted of studies of the fundamental dynamics, mode selectivity, IVR in highly excited polyatomic molecules, simulations of unimolecular reactions, the development of a new method for calculating rates for IVR-limited unimolecular reactions, simulations of RDX conformational changes in dense gases, and the development of a crystal model for RDX.

Understanding the fundamental dynamics of polyatomic molecules is crucial for reaching the long-term goal of this program. Chemists are interested in controlling chemistry, and to do so requires that a thorough knowledge of basic, elementary mechanisms of chemical processes. In the case of unimolecular reactions this essentially means understanding the rates and pathways by which energy is redistributed. During the early stages of this research program (*i.e.*, previous grant periods) we performed extensive studies of IVR. Perhaps the most important result of our studies (and those of others) is that when a particular mode or combination of modes of a molecule are highly excited the excitation energy flows into the other molecular modes along well-defined pathways. Yet, as many theoretical and experimental studies have shown, there is sufficiently rapid "randomization" of the excitation energy such that mode selective reaction is usually not observed. This has often been interpreted to mean that the dynamics of the reacting molecules are chaotic or ergodic, perhaps, in part, because studies have shown that the dynamics of triatomic molecules can be chaotic at energies well below dissociation thresholds. This coupled with the general observations of statistical behavior of reactions has led some to the conclude that all (or most) molecules, regardless of size, are undergoing chaotic motion when they react. This situation prompted us to carry out calculations to explore the fundamental nature of the dynamics of molecules above their reaction thresholds.

We computed power spectra for a variety of molecules (C_2H_4, CH_3ONO, and SiF_4) for a variety of conditions, including mode selective excitations, in our initial study.[8] The energies considered in the study extend to levels well above threshold. The classical trajectories used to obtain the power spectra were integrated for 10 ps. The results clearly show that the spectral mode identities are retained on this time scale (10 ps) at quite high energies. That is, even at energies well above the reaction threshold polyatomic molecules behave quasiperiodically. There is significant mode mixing, but it is not global – the IVR occurs, on this time scale, among subsets of the molecular modes. Or, put in other terms, the trajectories do not sample all the available phase space. These conclusions still apply

when there are significant numbers of dissociations during the time the trajectories were followed. In general, molecular vibrations are not chaotic at the dissociation limit. In fact, our results suggest that, except for special small molecules, molecules will undergo reaction at energies well below chaotic limits.

We followed up this first study with one in which we examined power spectra for RDX for various initial conditions.[9] We were particularly interested in determining the nature of the dynamics at levels of excitation corresponding to those in infrared multiphoton dissociation (IRMPD) experiments. The computed power spectra comprise robust, well-defined bands for the chemically distinct internal coordinates. The bands for individual coordinates are readily distinguishable in the power spectra although they are significantly broadened. Nevertheless, there is considerable mode mixing. That is, although the molecular vibrations retain their identities, they rapidly exchange energy. In fact, we found that this is true of the classical motions even at the zero-point energy level, and that the spectra for excitation energies corresponding to those in IRMPD experiments are not much different from those at the zero-point energy level. Furthermore, the spectral broadening in RDX is much greater than that observed for the smaller molecules in our first study.[8]

The observed enhanced line broadening in RDX may be due to the fact that it undergoes chair-to-boat conformational changes. Eigen,[10] in 1964, suggested that very fast reactions might affect vibrational spectra. If this is true, then the rates of reactions might be determined from vibrational line shapes, as is done from NMR spectra. There is, of course, and this is the main problem, a significant difference in the time scales for NMR and vibrations. We carried out a series of calculations to determine the influence of crossings of a transition state (*i.e.*, reactions) on mode mixing (power spectral line broadening and shifting). These studies were done for intramolecular isomerizations in HONO, methyl nitrite, and RDX.[11,12] We found that mode mixing is indeed enhanced by repeated crossings of a barrier. We attempted to calculate rates of reactions from the line widths, however, we were unable to obtain quantitatively accurate results although there was qualitative agreement with the rates obtained from the first-order decay curves. We found that different types of normal modes are affected differently by the crossings of the barrier; the extent of broadening depends on the nature of the mode. Thus, this causes ambiguity in the determination of the reaction rates from spectral line broadening.

We also explored the possibility of using a Fourier transform method to calculate mode-to-mode energy transfer rates in polyatomic molecules.[13] The method uses Fourier transforms of the time histories of local-mode bond energies. The method was tested for HONO and C_2H_2. The basic idea of the method is that frequencies at which the peaks in the spectra appear correspond to the average mode-to-mode rate coefficients for the IVR. Although the method is not easily applied, it was found to give IVR rates that agree with the total relaxation rates determined from first-order decay curves of the local-mode energies.

The nitramine of prime interest is RDX, and one of the goals in this work has been to develop an accurate PES for the unimolecular dissociation of RDX. We have, during the previous grant period, developed a new PES for RDX dissociation in the gas phase based on spectroscopic and thermodynamics data, some *ab initio* results from the literature, and assumed behavior for the forces between critical points on the surface.[14]

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This PES represents a refinement of our earlier one;[15] it is based similar functional forms and the values of the parameters were determined in a similar fashion.

We assumed, based on the IRMPD results of Zhao, Hintsa, and Lee,[16] that the primary decomposition reactions of RDX are triple bond-fission that breaks the ring into three methylene nitramine (CH_2NNO_2) molecules and simple N-N bond rupture to eliminate NO_2. Quantum chemistry calculations have predicted a range of values for the height of the energy barrier for the ring fission dissociation channel.[17] Since there is lack of agreement about the energy barrier to ring fission, we performed classical trajectory calculations on three PESs that are similar except for the barrier height for that reaction channel. The barrier height to the simple bond rupture is generally accepted to be in the range 45-50 kcal/mol (however, a recent *ab initio* calculation[17b] predicts it to be 34.2 kcal/mol); we used 48 kcal/mol in our models. We calculated unimolecular dissociate rates for PESs with barrier to the ring fission of 37, 56, and 71 kcal/mol. The value of 71 kcal/mol was considered because it is a prediction based on some *ab initio* studies[17a] available at the time (The recent calculations by Wu and Fried[17b] gives a value of 52.5 kcal/mol). Only the PESs with the 37 kcal/mol barrier to ring fission gives results in accord with the Zhao *et al.*[16] experiments. They reported the ratio of the rate of ring fission to that of the simple bond rupture to be about two. Our results are for an approximate PES and thus cannot be used to definitely determine the kinetic parameters (*e.g.*, barrier heights), however, our studies strongly indicate that the barrier to ring fission must be lower than that for simple N-N bond rupture in order to explain the conclusions of Zhao *et al.*[16]

One of the difficulties with using classical trajectory simulations to calculate reaction rates is that it is often impossible to carry out the trajectory integrations for sufficiently long times to observe reactions at energies of interest for making comparisons with experiments. In practice, trajectories are usually computed at energies greatly in excess of reaction thresholds, and then the results are extrapolated down to the experimental energy range. However, unimolecular reactions are limited by IVR at high energies while they tend to be statistical near threshold, and thus it is not straightforward to extrapolate the rates over large energy ranges.[5] In the statistical regime, the rates can be calculated by using a statistical theory such as RRKM or MCVTST.

We have carried out a series of studies[4-7] to better understand the fundamental nature of the dynamics of unimolecular reactions over wide energy ranges. One of the results of this work has been the development of a new method based on diffusion theory that can be used to predict rates in the non-statistical regime.[5-7] We have shown that MCVTST can be used for practical calculations of the statistical rates near threshold, trajectories for the rates at high energies, and IDDT at intermediate energies where trajectories calculations are not feasible but the reactions are nonstatistical.

The advantage of MCVTST is that the statistical rates can be calculated for general PESs. Thus, we can obtain the statistical rates for direct comparisons with trajectory-computed dynamical rates. We have used MCVTST to calculate the unimolecular dissociation rate coefficients for RDX over the energy range 170-450 kcal/mol,[4] thus spanning the range from the experiments of Zhao *et al.*[16] to that of our trajectory results[18] (200-450 kcal/mol). The MCVTST-computed branching ratio[4] at 170 kcal/mol is in excellent agreement with the value of Zhao *et al.*[16] Comparisons of the

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trajectory and MCVTST results show that there are significant dynamical effects at the higher energies when the reaction is IVR-limited.[4] That is, at high energies the trajectory rates are smaller than the statistical rates.

The practical difficulties of obtaining rates at the lower end of the energy range where there are still significant dynamical effects (on the order of 200 kcal/mol in the case of RDX), led us to explore the use diffusion theory. We have developed a practical method, *intramolecular dynamics diffusion theory* (IDDT), that is based on a kinetic Fokker-Planck equation that describes the dynamics as diffusion of phase space points. In practical applications of IDDT, short-time classical trajectories are used to determine the time dependence of the flow of energy between the reaction coordinate mode (subsystem 1) and the other (bath) modes (subsystem 2) of the molecule. This can be done with trajectories integrated for only a few femtoseconds, thus greatly diminishing the required computer time compared to that needed for a standard classical trajectory simulation. Our results for dimethylnitramine (DMNA) will be described here to illustrate the method.

To demonstrate the accuracy of the IDDT method for predicting the dynamical rates of chemical reactions we carried out calculations for the dissociation of DMNA using a model of the reaction in which only simple bond fission occurs: $(CH_3)_2N-NO_2 \rightarrow (CH_3)_2N\bullet + \bullet NO_2$.[6] Thus, the N-N bond stretching (which does not correspond to a normal mode) is taken to be the reaction coordinate. We integrated ensembles of 1000 trajectories for 1.2 fs for total energies of 250, 300, and 400 kcal/mol, and computed the rate of energy flow by monitoring the energy in the reaction coordinate. That is, we calculate the rate of spreading of an initially narrow distribution. The IDDT rates are quite close to the results obtained from a classical trajectory simulation, in fact, they are in quantitative agreement. The statistical (MCVTST) rates were also calculated, and, as expected, the dynamical rates are lower than the statistical rates. The IDDT method accurately predicts the nonstatistical dynamical effects.

It is worthwhile to again point out that the trajectory calculations to determine the IVR rates needed for IDDT calculations require very short integration times (on the order of femtoseconds) and thus the savings in computer time compared to that required for a standard classical trajectory calculation of the rate coefficient is significant. Furthermore, the same amount of computer time is required to calculate the rates for any total energy, while the cost in computer time for classical trajectory simulations drastically increases as the total energy decreases. Standard classical trajectory simulations may not even be feasible at energies at the lower end of the dynamical regime, while the IDDT method can be easily used to compute the rates there. However, at sufficiently low energies where the reaction is slow and statistical, the IDDT approach, which is based on the assumption that reaction is fast compared to IVR, is not valid. Then, the rate must be calculated by using a statistical theory, *e.g.*, MCVTST. The lower of the rates calculated by MCVTST and DDT is to be taken as the actual rate of reaction.

We have also applied IDDT to the reaction $H_3Si-SiH_3 \rightarrow 2\ SiH_3$.[5] The Si-Si stretch can be easily identified as the reaction coordinate. Due to the difference in masses of Si and H the Si-Si stretch is a good normal mode, thus the flow of energy between it and the other molecular modes which comprise the energy reservoir is slow. It is the kind of situation where it is expected that diffusion theory should provide a good description of the reaction dynamics. A large ensemble of trajectories were calculated to determine both

the statistical and non-statistical decay rates, and MCVTST calculations were also done to determine the statistical rates. The results of the various calculations are compared in Table I.

Table I. Values of the rate coefficients for $Si_2H_6 \rightarrow 2\ SiH_3$ computed by using classical trajectories, MCVTST, and diffusional theory at 400 kcal/mol.

Method	$k\ (s^{-1})$
Trajectory Simulation:	
Initial decay (statistical)	4.6×10^{12}
Long-time decay (non-statistical)	5.1×10^{11}
MCVTST (statistical)	4.4×10^{12}
IDDT (non-statistical)	4.6×10^{11}

However, the accuracy of the IDDT approach for the decomposition of DMNA is less obvious; the N-N stretch is not an isolated mode. The DMNA results show that the IDDT approach can be used for reactions where there is strong coupling of the reaction coordinate to the bath modes.

One of the long-term goals of this research program is to perform simulations of the multi-step chemical decomposition of RDX through the various intermediates to the final small molecular products. We have studied some of the steps in the decomposition. One of the initial products of the decomposition of cyclic nitramines is methylene nitramine, CH_2NNO_2 (MN). Working in collaboration with Dr. Betsy Rice at ARL, we have developed an accurate analytical PES, based on the *ab initio* results of Mowery *et al.*,[19] for the decomposition of this molecule.[20] The two primary decomposition reactions, simple N-N bond rupture to give H_2CN and NO_2 and concerted molecular elimination via a 5-center transition state to yield HONO and HCN, are competitive since the barrier heights differ by only a few kcal/mol. Microcanonical ensembles of classical trajectories were computed for energies ranging from 61 to 131 kcal/mol (including 27.5 kcal/mol zero-point energy). The computed rates show that the dominant reaction path is N-N bond fission, but at high energies the molecular elimination reaction becomes comparable to it. We also followed the trajectories in which HONO was formed to study the secondary reactions of this product. The HONO molecules dissociate mainly by N-O bond scission, however, some O-H bond rupture was observed.

The results of this study may not be directly comparable to the experimental results of Zhao *et al.*[16] since the initial conditions may not be the same. We studied microcanonical initial distributions, while the experimental observations are for the decomposition of MN produced by the dissociation of RDX. Zhao *et al.* concluded that MN decays primarily *via* concerted molecular elimination, while our model based on the *ab initio* calculations predicts that the simple bond fission is competitive with (actually, greater than) that reaction. It is possible that the MN formed in the IRMPD beam experiments is produced with a nascent non-statistical distribution of energy. In an early study of the reaction dynamics of RDX decomposition, we found that MN is produced

vibrationally hot.[15] We did not, however, attempt to examine the nature of the vibrational distributions nor determine the fate of the MN products. We plan to do this in the near future (see Section IV); that is, we will develop a consistent set of PESs that allow us to follow the decomposition of RDX through the dissociation of the initial products (including MN). This may help resolve this point concerning the mechanism. We have studied vibrational mode selectivity in MN and find that excitation of certain modes affect the branching ratio.[21]

One of the central interests in our work has been mode selectivity in chemical reactions, and the decomposition of MN presents an interesting case for exploring mode selective behavior because of the two dissociation pathways. The simple N-N bond rupture represents the type of reaction that has been extensively studied experimentally in efforts to observe mode specificity, and it presents the kind of problem that is likely responsible for the fact that significant mode selective behavior is not commonly observed. Most experiments are done using overtone pumping of an XH (X = C, O, or other heavy atom) in a molecule in which reaction involves the breaking of a bond between two heavy atoms. This requires that most of the excitation energy (usually on the order of 40 to 60 kcal/mol) flow from the high frequency XH mode to the low frequency reaction coordinate mode faster than to the other modes of molecules. However, concerted molecular elimination reactions involving hydrogen migration, such as that in the dissociation of MN, present a much more favorable case for mode selective chemistry. Here the excitation energy can be deposited directly into a mode involving the H-atom motion, thus making the competition between energy randomization and mode selective reaction more favorable to the latter. These arguments are evident in some of our earlier work, however, in our study of MN we did a thorough analysis of the factors that affect mode selective unimolecular reaction.

We used classical trajectories to study vibrational mode selectivity in the decomposition rates and branching ratio for the two channels in MN. We calculated rates for microcanonical statistical and for non-statistical (vibrationally excited normal modes) initial distributions. Comparisons of the mode selective rates with the statistical rate was used to determine the extent of selectivity. We also examined the basic causes of selectivity in the reactions by determining the extent of the coupling of each vibrational mode with the reaction coordinates. We did this by projecting the eigenvector of the vibrational mode onto the eigenvectors of the two reaction coordinates at points along the reaction paths. That is, we determined the extent of the projections all along the reaction paths. If a particular mode has large projections along the reaction coordinate and is not strongly coupled to the other modes in the molecule, then reaction should be significantly enhanced by its excitation. Our analysis shows that both conditions, the excited mode is strongly coupled to the reaction coordinate and they are both isolated from the rest of the modes, are necessary for mode selective reaction.

We have also performed some "preliminary" studies of RDX in "condensed phases." For example, we have performed molecular dynamics simulations of conformational changes (chair→boat) in RDX.[22] Rates and other quantities were calculated for RDX in isolation and in dense Xe gas. The results show that as the solvent concentration increases, the concentration of RDX in the boat conformation increases by a factor of ~4. The rate constant for the chair→boat inversion was calculated as a function

of the Xe density; at low concentrations the rate increases with increasing solvent density in accordance with Lindemann theory. As the concentration increases, the rate constant reaches a maximum, Kramer's turnover, and then decreases until at a much higher density it goes through a minimum. We propose to extend these studies to chemical reactions; *e.g.*, the unimolecular decomposition of RDX, to determine the influence of the solvent on the branching ratio for the ring- and bond-fission reactions.

We have developed an intermolecular potential that describes the structure crystal structure of α-RDX.[23] It is composed of pairwise atom-atom (6-exp) Buckingham interactions and charge-charge interactions. The parameters of the Buckingham repulsion-dispersion terms were determined through a combination of non-linear least-squares fitting to observed crystal structures and lattice energies and trial-and-error adjustment. Crystal packing calculations were performed to determine the equilibrium crystallographic structure and lattice energy of the model. There are no significant differences in the geometrical structures and crystal energies resulting from minimization of the lattice energy with and without symmetry constraints. Further testing of the intermolecular potential were done by performing symmetry-constrained isothermal-isobaric Monte Carlo simulations. The properties of the crystal (lattice dimensions, molecular orientation, and lattice energy) determined from Monte Carlo simulations at temperatures over the range 4.2 to 300 K indicate good agreement with experimental data. We also performed isothermal-isobaric molecular dynamics calculations at ambient pressure for temperatures ranging from 4.2 to 325 K. Crystal structures at 300 K are in excellent agreement with experiment (within 2% of lattice dimensions, and almost no rotational and translational disorder of the molecules in the unit cell). The space-group symmetry was maintained throughout the simulations. Thermal expansion coefficients were determined for the model, and are in reasonable accord with experiment.

We have developed a practical, multidimensional, semiclassical method for treating processes such as tunneling in large molecules.[24-29] This method incorporates tunneling effects in standard classical trajectory simulations, and thus all the degrees of freedom of a many-atom system are readily treated. Semiclassical methods have not proven very useful in general for practical problems since it is difficult (or even impossible) to rigorously apply them in for many dimensions. Our method is easily applied to problems such as proton tunneling in unimolecular or bimolecular reactions of large molecules. We have demonstrated its accuracy for various kinds of situations.[24-29] Comparisons with quantum mechanical results and experimental data show that the method is more accurate than other approaches.

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III. List of Publications and Technical Reports

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IV. Participating Scientific Personnel

The following is a list of the personnel who participated in the research described in this report:

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  Candee C. Chambers (Ph.D., 1994)
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